NOVEL CLEAR BEVERAGE OPTIONALLY ALCOHOLIC CONTAINING ANETHOL AND CLOUDY DILUTED BEVERAGE OBTAINED BY DILUTION

The present invention relates to clear beverage optionally alcoholic containing anethol which are intended to be diluted, causing clouding. The invention relates more particularly to aniseed-based spirits with a low alcohol level.

Pastis are aperitive beverages consisting of a clear solution of anethol in ethanol. The majority of pastis correspond to 2 g/l solutions of anethol in 45% v/v ethanol.

Among consumers there is a desire for beverages of this kind, based on anethol, whose alcohol content is, however, less than 45%; for example, beverages containing only 20% alcohol.

For reasons related to the organoleptic qualities of the beverage, it is not possible to reduce the concentration of anethol too greatly; it must remain close to 2 g/l. Under these conditions, it is not possible to dissolve 2 g/l of anethol in 20% alcohol; the immediate result is clouding, which is not commercially acceptable for this type of product. Furthermore, it is necessary to take into account the fact that aniseed-based beverages, although they are required to be clear in the bottle, must become cloudy on addition of water; that is, on dilution with approximately 5 volumes of water.

In fact, taking into account the solubility curve of anethol as a function of the alcohol level (figure attached, at 20°C), it appears impossible to dissolve more than about 200 mg of anethol/l in 20% alcohol and more than 400 mg/l in 30%. Above the solubility threshold, the anethol is partially in an insoluble form (oily droplets) and gives a cloudy/milky appearance to the mixture.

Patent Application FR-A-2 638 761 describes a clear ethanolic composition containing anethol, charac-

terized in that it consists of at least one aqueous-ethanolic medium containing from 10 to 30% ethanol v/v and from 1 to 3 g/l of anethol and, in addition, in an amount effective for keeping the composition clear, a surfactant or a mixture of neutral surfactants of formula $R-O-(CH_2-CH_2-O)_nH$, having the following characteristics:

- it is acceptable in human food,
- its HLB is $12 < HLB < 15$,
- the CMC is $10^{-1} > CMC > 10^{-3}$,

the cloud point being greater than 30°C for a nonionic surfactant and the Krafft temperature being less than 10°C for an ionic surfactant.

The object of the present invention is to provide a novel beverage having similar properties or advantageous properties relative to that described in Patent Application FR-A-2 638 761.

Another object of the present invention is to provide a clear beverage whose solubility threshold is greater, for a given volume of alcohol, than that indicated on the curve attached to the single figure.

Another object of the present invention is to provide a beverage which is stable over time.

Another object of the present invention is to provide a beverage which becomes cloudy when it is diluted with water, and does so as a function of its composition.

The invention therefore first provides a beverage optionally alcoholic containing anethol, characterized in that it comprises an effective amount of at least one phospholipid which is acceptable in human food, in order to improve the solubility of anethol in said beverage.

By "effective" amount is meant an amount sufficient to reduce the turbidity of nonalcoholic or slightly alcoholic beverages containing anethol.

The invention relates in particular to nonalcoholic or slightly alcoholic beverages.

By nonalcoholic beverage is meant, in accordance with legislation, a beverage whose alcohol content is less than 1.2%.

By slightly "alcoholic" are meant beverages whose alcohol level is less than 400 g/l, in particular less than 300 g/l.

Among these phospholipids, mention is made of the phospholipids present in lecithins or derivatives thereof, especially lysolecithins, of vegetable or animal origin. These phospholipids may be present in pure form or in the form of a mixture. Mention is also made of lecithins which are a complex mixture of phosphatides consisting primarily of phosphatidic acid, phosphatidylcholine, phosphatidylethanolamine, phosphatidylserine, lysophosphatidylcholine and phosphatidylinositol, in combination with varying amounts of other substances such as triglycerides, glycolipids, sphingolipids, fatty acids, and carbohydrates.

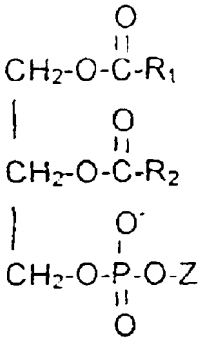
It is therefore possible to select either the abovementioned phospholipids or the lecithins containing these phospholipids.

Among the lecithins, mention is made of those of vegetable or animal origin (extracted from soya, eggs).

Among the latter, mention is made of lecithins having highly varied chemical characteristics: crude lecithins such as Epikuron 145®, phosphatidylcholine-enriched fractions such as Epikuron 200™, Ovothin 180 or Phospholipon 80®, enzymatically modified lecithins such as Epikuron 200 E™ and Sternpur™.

The concentration of the phospholipid or phospholipids, in particular of the lecithin or lecithins, is a function of the type of phospholipids selected and of the alcohol and anethol contents of the beverage.

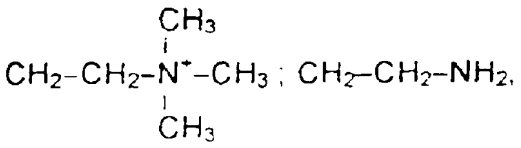
According to one variant, the phospholipids correspond to the formula indicated below:

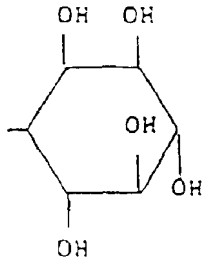


in which:

R_1 and R_2 are identical or different and are C_{14}-C_{22} fatty acid radicals,

Z is the hydrogen atom or a radical





As has already been specified, one of the features of the invention is to make it possible to obtain clear, slightly alcoholic aniseed-based beverages. For example, the turbidity is in particular less than 100 NTU.

In a beverage containing optionally a small amount of alcohol and an amount of anethol greater than the solubility threshold (as is the case of the compositions present in zone A of the attached curve), the anethol is in insoluble form (oily droplets) and gives a cloudy/milky appearance to the mixture. In zone B, the beverage is clear.

The clarity of the beverage according to the invention results from the fact that it is in the form of a submicron emulsion, or microemulsion, composed of nanosomes whose average diameter is less than 100 nm, of the type comprising an anethol-phospholipid phase in an aqueous, alcoholic or nonalcoholic phase.

A microemulsion is an emulsion in which the size of the particles is so low (in particular < 100 nm) that the particles are imperceptible to the eye; a clear phase is observed, comparable to a true solution but consisting of an emulsion.

The production of a microemulsion by one or more appropriate surfactants therefore makes it possible to increase the apparent solubility of the anethol with limited percentages of alcohol.

In other words, the emulsifiers make it possible to disperse the essential oil very finely to the point where a so-called "apparent" solubility is obtained (insoluble oil droplets invisible to the human eye).

The anethol contents in question are generally between 0.2 and 10 g/l, and preferably from 0.5 to 2 g/l, whereas the concentration of phospholipids will advantageously be between 0.4 and 30 g/l. The amount of surfactants will increase with the concentration of anethol. Consequently, the ratio by weight between the phospholipid and the anethol is preferably between 0.5 and 10.

The beverage according to the invention contains preferably between 8 to 400 g/l of ethanol; preferably, it is slightly alcoholic, between 40 and 300 g/l of ethanol.

With a view to good quality (fineness of the emulsion) and good stability, all of the components of the formula must be mineralized to the least extent possible and, in particular, must be poorest in divalent cations.

In certain cases, perfect clarity is obtained only after having subjected the emulsion to an appropriate mechanical treatment. The purpose of this treatment is to reduce the droplet size of the emulsion and thus to increase the clarity and the physicochemical stability. Various treatments are found to be satisfactory. By way of example, high-pressure treatments (high-pressure homogenization), or high-speed shear

treatments (high-speed mixer/helical grinder) fulfill this purpose.

Whatever the treatment employed, it can be applied either to the products or to concentrated formulas with higher anethol and lecithin contents, which will be diluted subsequently.

The treatments depend on the formula in question; in homogenization, the pressures employed can vary from 20 to 150 Mpa (from 200 to 1500 bars) with one or more cycles; in shear treatment, the application time depends on the volume treated.

According to the composition of the beverage and the type of phospholipid, especially lecithin, the system appears more or less subject to oxidative mechanisms which result in the incidence of unpleasant olfactory notes or unpleasant tastes. These undesirable mechanisms are prevented/retarded by virtue of the incorporation into the formula of substances which have antioxidant properties. These can be pure molecules or plant extracts containing antioxidant principles. Numerous substances fulfill this function. By way of example, it is possible to employ the following elements: tocopherols, ascorbyl palmitate, tea extracts (green black or others), rosemary extracts or sage extracts. The doses employed are a function of the concentration of active principle and of its effectiveness; of the content and nature of the lecithin in question; of the alcohol content, of the treatments applied to the emulsion (high pressures, etc.).

The invention is notable in that the emulsion will be required to exhibit clouding as a consequence of its destabilization when an appropriate aqueous solution is added.

Whatever the emulsion produced, it will exhibit clouding by dilution if the diluent is acidic.

On the other hand, if it is desired to obtain immediate clouding by dilution with a nonacidic aqueous liquid, which constitutes an advantageous variant, the

diluent will have to include one or more mineral dications such as magnesium, calcium, manganese.

In this case, it is desirable for the beverage according to the invention to comprise one or more compounds which give rise to and/or accelerate the destabilization of the emulsion at the time of dilution, in particular.

Phenolic compounds fulfill this function appropriately, and the following can be employed by way of example: catechins, gallocatechins, tannins, condensed tannins, gallic tannins, ellagitannins and derivatives (gallic esters, dimers, oligomers, theaflavins, thearubigins, catechin, epicatechin, epigallocatechin, gallocatechin and their mono- and digalloyl esters, etc.), stilbenes, flavonoids (phloretin and derivatives, etc.).

In this context, it is possible to employ the pure molecules or else a plant extract/concentrate containing one or more of these structures (e.g.: tea leaf extracts (green, black or oolong), ginkgo biloba, fruit extracts: apple, aubepine, guarana, grape, elder; wood, bark, peel, roots and nuts: oak tannins, oak-apple tannins, gambir tannins, grape seeds, Chinese rhubarb roots, clove, cinnamon, licorice, cola, etc.).

In all cases, the plant extract must be treated before incorporation into the formula, so as to remove all of the divalent cations, by using a cation exchange resin, for example.

A single plant extract may possess both antioxidant properties and those of a clouding "catalyst" on dilution (e.g., tea extract). In the converse case, a number of extracts can be combined. Although the presence in the beverage of phenolic extract or compound is indispensable to the appearance of the clouding when dilution is carried out with water (or with a nonacidic beverage), this clouding is linked to the addition of divalent cations (primarily Ca, Mg, Mn) which are present in the diluent liquid. Therefore, a significant content of one and/or other of these dications in the

diluent medium is indispensable to the mechanism of appearance of cloudiness in the beverage. Therefore, particularly mineralized waters appear favorable to the mechanism.

Consequently, the beverage according to the invention will contain essentially no dications (magnesium, calcium, manganese) whereas the diluent medium will preferably comprise them. The term "essentially" indicates that the beverage will not contain a sufficient quantity of dications to adversely affect the clarity.

The beverage preferably comprises per liter:

- from 8 g to 400 g of ethanol, advantageously from 40 to 300 g of ethanol,
- from 0.2 to 10 g of anethol
- from 1 to 30 g of phospholipids
- water q.s. to 1 l, at 20°C

an effective amount of substances which destabilize the emulsion, especially phenolic compounds, when said beverage is diluted with water containing a sufficient amount of the divalent food cations, one or more antioxidant substances, optionally sugar, especially sucrose, fructose, glucose, maltose, lactose.

The measurement is made at 20°C, it being understood that the proportions will vary in a known manner at a different temperature.

The invention additionally relates to the cloudy alcoholic or nonalcoholic beverages obtained by diluting a beverage according to the invention in particular with a mineralized water.

The examples below illustrate the invention.

EXAMPLES

The beverages of the following examples are produced either by high-pressure treatment ("Lab 40" from APV-Gaulin; "Pony" from Westfalia Separator) or, for low-volume laboratory tests, by treatment with a high-speed grinder/mixer (Ultra-Turrax T25 Janke &

Kunkel at 24,000 rpm for volumes of approximately 10 ml; Polytron Kinematica at maximum speed for volumes of the order of a liter; Silverson L4RT mixer for volumes greater than a liter).

The sizes of the anethol droplets emulsified in this way are measured by laser granulometry (Malvern "Zetamaster" granulometer) directly without diluting the beverage.

The lecithins and fractions (of egg and soya) employed hereinbelow were supplied:

by Lucas-Meyer:

Epikuron E145 (containing 50% phosphatidylcholine)

Epikuron E200E (consisting essentially of lysophosphatidylcholine)

Ovothin 180 (containing 80% phosphatidylcholine)

and by Stern/Nattermann:

Phospholipon 80 (containing 80% phosphatidylcholine)

SternpurE (consisting essentially of lysolecithins)

Example 1

7.5 g of anethol and 10 g of Epikuron 145 are dissolved in 1050 g of 96° alcohol. This solution is added to demineralized water (q.s. to 5 l) with stirring. The pre-emulsion obtained is subjected to an APV-Gaulin homogenization treatment: 80 Mpa (800 bars); 3 pressure cycles. This beverage does not cloud when it is diluted with water; it clouds when diluted with an acidic beverage of the tonic, cola, or fruit-based acidic beverage type.

Example 2

15 g of anethol and 30 g of Phospholipon 80 are dissolved in 2100 g of 96° alcohol. This solution is added to demineralized water (q.s. to 10 l) with stirring. The pre-emulsion obtained is subjected to a

Westfalia Separator homogenization treatment: 1 cycle of 100 Mpa (1000 bars). The average diameter of this emulsion is 10 nm. By way of example, a turbidity of 15 NTU is measured on this type of beverage.

On dilution, this beverage behaves as in Example 1.

Example 3

7.5 g of anethol and 10 g of Epikuron 145 are dissolved in 1050 g of 96° alcohol. This solution is added with stirring to demineralized water containing 1.2 g of catechins extracted from decaffeinated green tea or 75 ml of an aqueous-alcoholic extract of black tea, without dications (water: q.s. to 5 l). The tea extracts here act as antioxidant and clouding catalyst. The pre-emulsion obtained is subjected to an APV-Gaulin homogenization treatment: 80 Mpa (800 bars); 3 pressure cycles. The average diameter of the emulsion produced is 50 nm, and it therefore appears to be relatively clear. With the two types of tea, the beverage clouds when it is diluted with water of the "Evian" type or with an acidic beverage, of the tonic, cola or fruit-based acidic beverage type.

Example 4

10 g of anethol and 20 g of Phospholipon 80 are dissolved in 1050 g of 96° alcohol. This solution is added with stirring to demineralized water containing 50 ml of aqueous green tea extract (antioxidant and clouding catalyst), which has been freed of divalent cations by resin exchange (water: q.s. to 5 l). The pre-emulsion obtained is subjected to a Westfalia Separator homogenization treatment 100 Mpa (1000 bars); 2 pressure cycles. The average diameter obtained is 25 nm. The beverage is clear, slightly more "bright" to the eye than in Example 3. The turbidity measured on this product is less than 50 NTU. The behavior on dilution is similar to that described in Example 3.

N.B.: The divalent cations can be removed from any ingredient forming part of the composition of the beverage (tea extract, rosemary, etc.) by treatment, for example, on a cation exchange column in H^+, Na^+ or K^+ form.

Example 5

1.5 g of anethol and 3 g of Phospholipon 80 are dissolved in 210 g of 96° alcohol. This solution is added with stirring to demineralized water containing 0.3 g of oak-apple tannins or 0.5 g of oak tannins (clouding catalyst) and 0.5 g of aqueous rosemary extract (antioxidant), from which divalent cations have been removed by exchange on ion exchange resin (water: q.s. to 1 l). The pre-emulsion obtained is subjected to a Polytron treatment for 5 minutes. The behavior of this beverage on dilution is as in Example 3.

Example 6

0.75 g of anethol and 1.5 g of Phospholipon 80 are dissolved in 105 g of 96° alcohol. This solution is added with stirring to demineralized water containing 6.25 ml/l of phenol-rich apple concentrate (clouding catalyst), neutralized to pH = 7 (water: q.s. to 0.5 l). The pre-emulsion obtained is subjected to a Polytron treatment for 2 minutes. The beverage thus produced, without demineralization of the apple extract, does not appear to be of outstanding clarity (turbidity: 200 NTU) owing to the presence of the divalent cations from the apple. On dilution, it clouds under the same conditions as Example 3. If this same formula is produced under the same conditions but with a low-phenol apple concentrate, the formula does not exhibit clouding when diluted with water of "Evian" type and, like Examples 1 and 2, it clouds solely on addition of an acidic liquid.

If the beverage is produced with a phenol-rich apple extract which is devoid of divalent cations, the

emulsion is clear (turbidity: 82 NTU) and clouds under the same conditions as Example 3.

Example 7

1.4 g of anethol and 2.7 g/l of Epikuron 200E are dissolved in 294 g of 96° alcohol. This solution is added with stirring to demineralized water containing 0.360 g of aqueous green tea extract (clouding catalyst and antioxidant), from which divalent cations have been removed by resin exchange (water: q.s. to 1 l). The pre-emulsion obtained is subjected to a Polytron treatment for 5 minutes. The beverage produced is relatively clear and clouds on dilution under the same conditions as Example 3.

Example 8

1.4 g of anethol are dissolved in 294 g of 96° alcohol. This solution is added with stirring to demineralized water containing 1.3 g of Sternpur E and 50 g of sucrose in dissolved form (water: q.s. to 1 l). The pre-emulsion obtained is obtained by virtue of a Silverson L4RT mixer at maximum speed. The formula is clear and does not cloud when diluted with Evian water (cf. Example 1).

Example 9

0.15 g of anethol and 0.8 g of Phospholipon are dissolved in 12.6 g of 96° alcohol. This solution is added with stirring to demineralized water containing 0.12 g of catechins (clouding catalyst and antioxidant) extracted from green tea and devoid of dications (water: q.s. to 0.1 l). The pre-emulsion obtained is subjected to a Polytron treatment for 2 minutes. The beverage thus produced is clear (turbidity: 60 NTU) and its behavior on dilution is as in Example 3.

Example 10

0.1 g of anethol and 0.3 g of Phospholipon are dissolved in 4.2 g of 96° alcohol. This solution is added with stirring to demineralized water containing 2 ml of green tea extract (clouding catalyst and antioxidant) (water: q.s. to 0.1 l). The beverage thus produced is clear (turbidity: 87 NTU) and its behavior on dilution is as in Example 3.

Example 11

0.1 g of anethol and 0.3 g of Phospholipon are dissolved in 4.2 g of 96° alcohol. This solution is added with stirring to demineralized water containing 2 ml of green tea extract (clouding catalyst and antioxidant) (water: q.s. to 0.5 l). The beverage thus produced is clear. It clouds slightly on dilution with water of the "Evian" type or with an acidic beverage of the "tonic" or "cola" type, etc., owing to its low anethol content.

Example 12

37.5 g of anethol and 96 g of Phospholipon 80 are dissolved in 1050 kg of 96° alcohol. This solution is added with stirring to demineralized water (q.s. to 5 l). This emulsion base containing 25% v/v of alcohol concentrated 5 times is subjected to a double homogenization treatment at 1000B (Westfalia Separator). This clear emulsion (turbidity: 25 NTU) exhibits an average diameter of anethol droplets of 10 nm.

This base is used dilute:

- for example, 0.1 l of this base to which 20 ml of guarana extract or else of cola extract free from minerals (clouding factor) and 0.2 g of rosemary extract, from which divalent cations have been removed by resin exchange (antioxidant) are added, are diluted in a water-alcohol mixture containing 25% alcohol (q.s. to 1 l).

- or else 1.33 l of concentrated base, 50 ml of green tea extract (antioxidant and clouding factor) and 100 ml of licorice extract from which divalent cations have been removed by resin exchange are diluted in a 25% water alcohol mixture to 5 l.

On dilution, these two formulations behave as in Example 3.